The role of Zhang-Rice singlet-like excitations in one-dimensional cuprates

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We present the first calculation of the electron-energy loss spectrum of infinite one-dimensional undoped CuO_3 chains within a multi-band Hubbard model. The results show good agreement with experimental spectra of Sr_2CuO_3. The main feature in the spectra is found to be due to the formation of Zhang-Rice singlet-like excitations. The **q**-dependence of these excitations is a consequence of the inner structure of the Zhang-Rice singlet. This makes the inclusion of the oxygen degrees of freedom essential for the description of the relevant excitations. We observe that no enhanced intersite Coulomb repulsion is necessary to explain the experimental data.

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Recently, charge excitations in the quasi one-dimensional compound Sr_2CuO_3 have been investigated both experimentally[1–3] and theoretically.[2–6] Sr_2CuO_3 is composed of chains formed by CuO_4 plaquettes which share the corner oxygens. The magnetic properties of these chains have been successfully described using a one-dimensional spin-$\frac{1}{2}$ Heisenberg antiferromagnet.[7–9]

Experimentally, the electron-energy loss spectrum (EELS) of Sr_2CuO_3[3] shows several interesting features (see Fig. 1): For small momentum transfer ($q = 0.08$ Å^{-1}) parallel to the chain direction, one observes a broad peak around 2.4 eV energy loss, and two relatively sharp, smaller maxima at 4.5 and 5.2 eV. With increasing momentum transfer, the lowest-energy feature shifts towards higher energy, reaching 3.2 eV at the zone boundary ($q = 0.8$ Å^{-1}). Thereby its spectral width decreases. In addition, the peaks at 4.5 and 5.2 eV lose spectral weight as the momentum transfer increases, while some less well-defined structures emerge around 6 eV.

So far, these results have been compared only to calculations in an extended one-band Hubbard model.[3,6] From this comparison, Neudert *et al.*[3] concluded that in Sr_2CuO_3 there is an unusually strong intersite Coulomb repulsion V: In the one-band model it is of the order of 1 eV. It is argued that this large value of V allows for the formation of excitonic states which are observed in the experiment. One of the aims of this paper is to show that no intersite Coulomb repulsion is necessary to explain the basic features of the experiment, if the O degrees of freedom are taken into account within the framework of a multi-band Hubbard model.

We investigate the EELS spectrum of a one-dimensional CuO_3 chain system, using a multi-band Hubbard Hamiltonian at half-filling. In the hole picture this Hamiltonian reads

$$\begin{aligned} H = \Delta \sum_{j\sigma} n^p_{j\sigma} + U_d \sum_i n^d_{i\uparrow} n^d_{i\downarrow} \\ + t_{pd} \sum_{<ij>\sigma} \phi^{ij}_{pd} (p^\dagger_{j\sigma} d_{i\sigma} + h.c.) \\ + t_{pp} \sum_{<jj'>\sigma} \phi^{jj'}_{pp} p^\dagger_{j\sigma} p_{j'\sigma} \ , \end{aligned} \tag{1}$$

where $d^\dagger_{i\sigma}$ ($p^\dagger_{j\sigma}$) create a hole with spin σ in the i-th Cu $3d$ orbital (j-th O $2p$ orbital), while $n^d_{i\sigma}$ ($n^p_{j\sigma}$) are the corresponding number operators. The first and second term in Eq. (1) represent the atomic part of the Hamiltonian, with the charge-transfer energy Δ, and the on-site Coulomb repulsion U_d between Cu $3d$ holes. The last two terms in Eq. (1) are the hybridization of Cu $3d$ and O $2p$ orbitals (hopping strength t_{pd}) and of O $2p$ orbitals (hopping strength t_{pp}). The factors ϕ^{ij}_{pd} and $\phi^{jj'}_{pp}$ give the correct sign for the hopping processes. Finally, $\langle ij \rangle$ denotes the summation over nearest neighbor pairs.

The loss function in EELS experiments is directly proportional to the dynamical density-density correlation function $\chi_\rho(\omega, \mathbf{q})$,[10] which depends on the energy loss ω and momentum transfer $\mathbf{q}$. $\chi_\rho(\omega, \mathbf{q})$ is calculated from

$$\chi_\rho(\omega, \mathbf{q}) = \frac{1}{i} \int_0^\infty dt \ e^{-i\omega t} \langle \Psi | [\rho_{-\mathbf{q}}(0), \rho_{\mathbf{q}}(t)] | \Psi \rangle \ , \tag{2}$$

with

$$\rho_{\mathbf{q}} = \sum_{i\sigma} n^d_{i\sigma} e^{i\mathbf{q}\mathbf{r}_i} + \sum_{j\sigma} n^p_{j\sigma} e^{i\mathbf{q}\mathbf{r}_j} \ , \tag{3}$$

where $|\Psi\rangle$ is the ground state of H, and $\rho_{\mathbf{q}}$ is the Fourier transformed hole density. The ground state $|\Psi\rangle$ is approximated as follows:[11] We start from a Néel-ordered state $|\Psi_N\rangle$ with singly occupied Cu $3d$ orbitals (with alternating spin direction) and empty O $2p$ orbitals. Fluctuations are added to $|\Psi_N\rangle$ using an exponential form

$$|\Psi\rangle = \exp\left(\sum_{i\alpha} \lambda_\alpha F_{i,\alpha} \right) |\Psi_N\rangle \ . \tag{4}$$

The fluctuation operators $F_{i,\alpha}$ describe various delocalization processes of a hole initially located in the Cu $3d$ orbital at site i, where a summation over equivalent final sites takes place.[11] The parameters λ_α in Eq. (4) describe the strength of the delocalization processes and are determined self-consistently by solving the system of equations $\langle \Psi | \mathcal{L} F^\dagger_{0,\alpha} | \Psi \rangle = 0$, where $\mathcal{L}$ is the Liouville operator, defined as $\mathcal{L}A = [H, A]$ for any operator A. These equations have to hold if $|\Psi\rangle$ is the ground state of H.

Using Eqs. (2) and (4), we calculate the EELS spectrum by means of Mori-Zwanzig projection technique.[12] For a set of operators D_μ, the so-called dynamical variables, the following matrix equation approximately holds

$$\sum_\gamma \left[z\delta_{\mu\gamma} - \sum_\eta \langle\Psi|D_\mu^\dagger \mathcal{L} D_\eta|\Psi\rangle \left(\langle\Psi|D_\eta^\dagger D_\gamma|\Psi\rangle\right)^{-1} \right] \times \\ \times \langle\Psi|D_\gamma^\dagger \frac{1}{z-\mathcal{L}} D_\nu|\Psi\rangle = \langle\Psi|D_\mu^\dagger D_\nu|\Psi\rangle \ , \quad (5)$$

where $z = \omega + i0$. In Eq. (5) the set of dynamical variables was assumed to be sufficiently large so that self-energy contributions can be neglected. The set $\{D_\mu\}$ contains the dynamical variable $D_0 = \rho_{\mathbf{q}}$. Therefore, by solving Eq. (5), an approximation for Eq. (2) can be obtained. Besides D_0, the set includes $D_\alpha = \rho_{\mathbf{q}} F_{0,\alpha}$ for all α. The $F_{0,\alpha}$ are the fluctuation operators used in the ground state Eq. (4), without the summation over equivalent final sites. We use altogether 12 dynamical variables and observe good convergence of the spectral function.

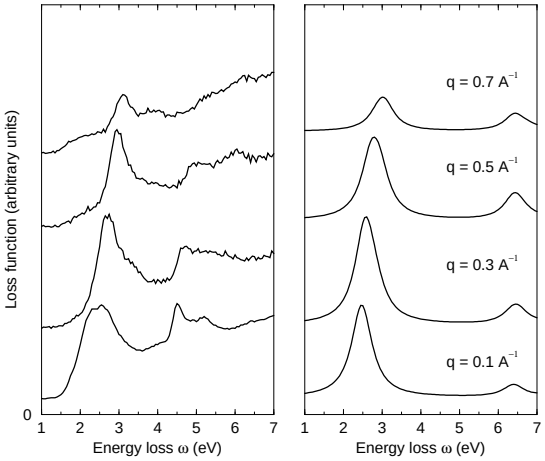

FIG. 1. Comparison of experimental data for Sr_2CuO_3 (left), taken from Ref. 3, and the present theoretical results for the one-dimensional multi-band Hubbard model (right). The theoretical line spectra have been convoluted with a Gaussian function of width 0.1 eV. For details see the text.

In Fig. 1 the obtained results are compared to the experimental spectra from Ref.[3]. The parameters in the Hamiltonian are chosen as follows: $U_d = 8.8$ eV and $t_{pp} = 0.65$ eV are kept constant at typical values.[13] The values of $\Delta = 4.3$ eV and $t_{pd} = 1.5$ eV have been adjusted to obtain the correct position of the lowest energy feature at 2.5 eV for $q = 0.01$ Å^{-1}, and at 3.1 eV for $q = 0.7$ Å^{-1}. Thus, we effectively use only two free parameters. It is found that the value of Δ dominates the excitation energy, which increases with increasing Δ. The dispersion of the peak depends mainly on t_{pd} with increasing dispersion for increasing hopping parameter. As compared to the standard value 1.3 eV,[13] $t_{pd} = 1.5$ eV is slightly enhanced, in agreement with recent results of band structure calculations.[14]

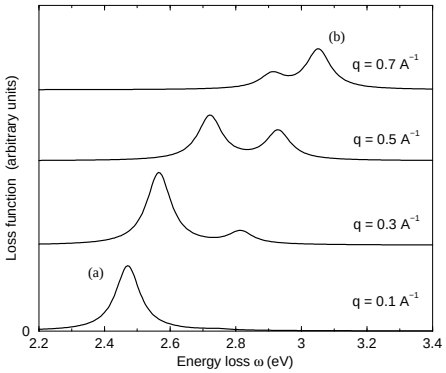

FIG. 2. The theoretical results for the dominant excitation at $2.4 - 3.1$ eV with a broadening of 0.02 eV. The momentum dependence of the spectrum is due to two different effects. First, with increasing $\mathbf{q}$ the spectral weight shifts from excitation (a) to (b). Second, the energies are $\mathbf{q}$-dependent. Both effects contribute to about one half of the full momentum dependence.

The theoretical spectra consist of two excitations. The dominant excitation is at 2.45 eV for $q = 0.1$ Å^{-1}, and shifts to 3.05 eV for $q = 0.7$ Å^{-1}. Besides, a second excitation appears at 6.4 eV which has no dispersion.

The low energy peak structure is shown in more detail in Fig. 2, where a smaller peak broadening has been used. As will be explained below, mainly two different Zhang-Rice singlet-like excitations[15] lead to this peak structure. The $\mathbf{q}$-dependence of the spectrum is due to two effects. Firstly, one observes a shift of spectral weight with increasing $\mathbf{q}$ between two excitations labelled with (a) and (b) in Fig. 2. Secondly, with increasing $\mathbf{q}$ the energies of the two peaks shift to higher values.

The shift of spectral weight can be attributed to different delocalization properties of the two final states. The excited state (a) in Fig. 2 which dominates the spectrum for small momentum transfer is rather extended, see Fig. 3(a). This state has a rather small probability for the hole at its original plaquette. With increasing $\mathbf{q}$ the spectral weight shifts to another excited state, shown in Fig. 3(b), with a higher probability for the hole on its original Cu-site. This means that the character of the excitation changes from an extended to a more localized one, while still forming a Zhang-Rice singlet.

This behavior can be understood by analyzing the relevant expectation values in Eq.(5). For small values of $\mathbf{q}$ the frequency term $\langle\Psi|D_\mu^\dagger \mathcal{L} D_\nu|\Psi\rangle$ can be approximated by expanding $e^{i\mathbf{qr}} \approx 1 + i\mathbf{qr}$ in Eq. (5). This gives $\langle\Psi|F_{0,\mu}^\dagger \mathcal{L} F_{0,\nu}|\Psi\rangle \times \mathbf{q}(\mathbf{r}_\mu - \mathbf{r}_\nu)$ which is proportional to the fluctuation distance, thus favoring far-reaching excitations. This picture changes for large values of $\mathbf{q}$, where stronger oscillations of the phase factor lead to a cancelation of extended excitations. The result is a transfer of

spectral weight from delocalized towards more localized excitations with increasing **q**.

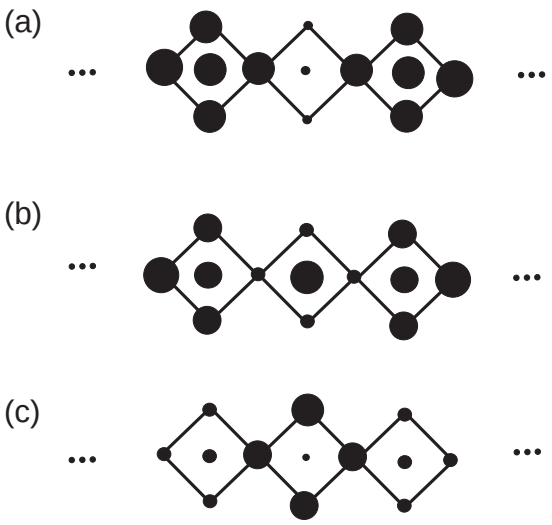

FIG. 3. Hole delocalization properties of different excited states. Larger (smaller) dots symbolize a larger (smaller) density of the hole originally located at the central plaquette. States (a) and (b) are Zhang-Rice singlet-like excitations with different delocalization properties. Excitation (a) has the largest spectral weight for small **q**, whereas excitation (b) has dominant spectral weight for large **q**, see also Fig. 2. Part (c) shows the local excitation at 6.4 eV, where the hole surrounds the central Cu site.

The **q**-dependence of the energies, on the other hand, is a consequence of the inner structure of the Zhang-Rice singlet-like excitations. In both excitations (a) and (b) a hole hops onto the Cu site of its nearest neighbor plaquette, see Fig. 3. Due to the Coulomb repulsion U_d, the hole which had originally occupied this Cu site is pushed away onto the surrounding O sites. Depending on the direction of this delocalization, this process leads to a **q**-dependence of the excitation energy.

Next, we want to stress that the claim in[3] for the one-band Hubbard model that only the inclusion of the next-neighbor repulsion leads to the possibility of the formation of an excitonic state is not consistent with our results. In the one-band model such a repulsion leads to a binding energy of empty and doubly occupied sites due to the reduction of neighboring interactions. This binding energy is proportional to V. However, as can be seen from exact diagonalization calculations in the one-band model,[16] the intersite repulsion mainly leads to an energy shift of the EELS spectra. Thus, the parameter V in the one-band model serves only to adjust the energetical position of the spectra, and is not necessary in more realistic models. In the multi-band model, the formation of an exciton is only driven by the energetically favored formation of a Zhang-Rice singlet, and no further inclusion of next-neighbor repulsion is necessary.

The important role of the Zhang-Rice singlet formation has been studied previously also in an effective model for excitons in the CuO_2 plane.[17] Like the one-band model, this effective model neglects inner degrees of freedom of the Zhang-Rice singlet. If this model is reduced to the CuO_3 chain, **q**-dependent energies are only possible for a non-vanishing O on-site Coulomb repulsion $U_p \neq 0$. In contrast to these results, we find **q**-dependent energies for $U_p = 0$. As described above this effect cannot be explained in a model which neglects the inner structure of the singlet.

Thus, our results show that both an inclusion of the O-sites and a complete description of the excitation is necessary to obtain the full dispersion. The O-sites are essential for the correct description of the different characters of the singlet excitations, which leads to the shift of spectral weight from one excitation to another. On the other hand, taking account of the inner degrees of freedom of the Zhang-Rice singlet leads to the **q**-dependence of the energies.

The results of the projection technique do not correctly describe the experimentally observed width of the peak for small momentum transfer. A possible explanation is that not all excitations are included in the projection space. The above discussion suggests that the width should be due to the presence of additional delocalized excitations. Processes which are neglected in the present calculation involve less important multiple excitations of holes beyond their original plaquette.

Finally, although they are not the focus of this paper, we discuss some high-energy features. The excitation at 6.4 eV in the theoretical spectra is due to a local process on the plaquette itself. Here, the hole is excited to the surrounding O sites, without leaving its original plaquette, see Fig. 3(c). The energy of this structure does not shift as a function of momentum transfer. Once again, a transfer of spectral weight towards this localized excitation with increasing values of **q** is observed. The plaquette excitation has a highly local character. Therefore, its spectral weight increases as a function of **q** compared to the more delocalized Zhang-Rice singlet excitations. For small **q** the spectral weight of the plaquette peak is about 6 times smaller than that of the Zhang-Rice peak. As **q** increases, this ratio increases to about one half. One should note that the experimental spectra show no obvious features above 6 eV. However, since many different orbitals may contribute in this energy range, we cannot expect a realistic description using a model that contains only Cu $3d$ and O $2p$ orbitals. This applies also to the experimental structure around 4.5 eV for small momentum transfer, which is not described by the present model. We assume that this feature is due to excitations which involve Sr orbitals, as has been argued before.[3]

In comparison with earlier works on Cu$2p_{3/2}$ X-ray photoemission spectroscopy using the same theoretical approach,[18] we find that the character of the excitations in both experiments is very similar. Zhang-Rice singlet

and local excitations play an important role. In both experiments the dominant excitation at low energies is associated with a Zhang-Rice singlet formation.

In conclusion, we have carried out the first calculation of the EELS-spectrum for the one-dimensional CuO_3 chain by using a multi-band-Hubbard model. Our results are in good agreement with experimental results for Sr_2CuO_3. We find that the main feature in the spectra is due to the formation of Zhang-Rice singlet-like excitations. The momentum dependence of the spectrum is due to two effects. First, there is a shift of spectral weight from less localized to more localized final states. Second, the excitation energies are **q**-dependent. This **q**-dependence is found to be a consequence of the inner structure of the Zhang-Rice singlet. Therefore, the inclusion of the O degrees of freedom is essential for the description of the relevant excitations. This has two important consequences. Firstly, only a multi-band model allows the correct description of charge excitations. And, secondly, if a multi-band model is used, no intersite Coulomb repulsion is necessary. Furthermore, we observe the existence of a local excitation at large **q**-values.

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